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茜草乔木酮乙和丙的结构

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摘要 从小红参（*Rubia yunnanensis*）中分离鉴定了2个新的乔木烷型三萜，分别命名为茜草乔木酮乙和丙（rubiarbonone B，C）。用光谱和化学方法证明它们的结构分别为：7β，19α，28－三羟基乔木－9（11）－烯－3－酮和28－乙酰氧基－7β，19α－二羟基乔木－9（11）－烯－3－酮。

关键词 小红参，茜草乔木酮乙，茜草乔木酮丙
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Structures of Rubiarbonone B and C

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Abstract From the roots of *Rubia yunnanensis*, two new arborane type triterpenoids, rubiarbonone B and C were isolated and their structures were elucidated as 7β, 19α, 28－trhydroxyarbor－9(11)－en－3－one and 28－acetoxyl－7β, 19α－dihydroxyarbor－9 (11) －en－3－one respectively by spectral and chemical methods.

Key words *Rubia yunnanensis*, Rubiarbonone B, Rubiarbonone C

We previously reported the isolation of new antitumor glycocyclohexapeptides (Zao *et al*, 1993a; He *et al*, 1993a; He *et al*, 1993b) and new arborane type triterpenoids (Zou *et al*, 1993b) from the roots of *Rubia yunnanensis*. Further study on the plants resulted in the isolation of two new arborane type triterpenoid ketones named rubiarbonone B and C respectively. In this paper we report the structure elucidation of these two compounds.

RESULTS AND DISCUSSION

Methanol extract of *Rubia yunnanensis* was dissolved in methanol and water (1:1), partitioned with petroleum ether and then chloroform. The solvent of chloroform layer was removed in vacuo and the residue was separated with silica gel column chromatography. Repeated silica gel chromatography and reverse phase chromatography resulted in the isolation of the two ketones rubiarbonone B and C.

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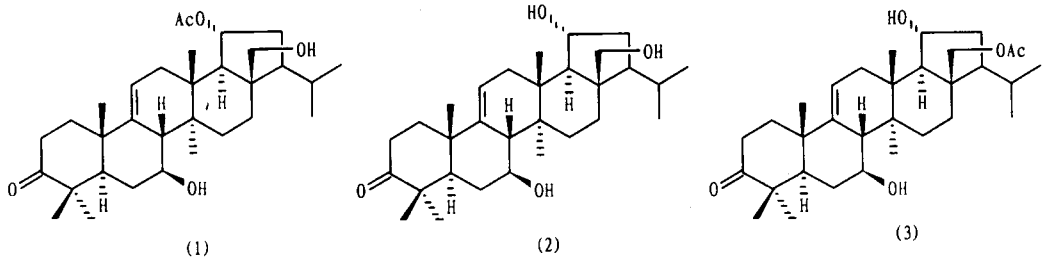

Fig 1　The structures of (1) ~ (3)

Table 1　^{13}C NMR data of (1) ~ (3)

C	(1)	(2)	(3)	C	(1)	(2)	(3)
1	37.40	37.30	37.36	18	56.32	60.00	59.58
2	35.18	35.18	35.15	19	74.75	70.72	69.33
3	215.22	215.26	215.18	20	40.43	43.52	42.62
4	47.44	47.43	47.35	21	57.61	58.14	57.51
5	49.91	49.90	49.89	22	30.25	30.79	31.11
6	34.44	34.48	34.44	23	25.42	25.42	25.40
7	71.58	71.62	71.61	24	21.12	21.09	21.06
8	49.30	49.38	49.20	25	22.01	21.02	22.01
9	146.41	146.12	146.28	26	16.97	17.20	17.13
10	39.49	39.39	39.41	27	16.35	16.78	16.64
11	118.01	118.60	118.27	28	63.22	62.98	64.80
12	36.60	37.72	37.23	29	23.09	23.45	22.94
13	38.12	38.44	38.18	30	23.31	23.66	23.48
14	40.28	40.30	40.07	Ac - 19	21.76		
15	33.05	33.06	32.33		170.90		
16	33.56	33.39	32.53	Ac - 28			21.06
17	48.41	49.03	47.42				170.72

Rubiarbonone B (2), $C_{30}H_{48}O_4$ (M^+ at m/z 472), colorless needles, mp 155 ~ 157 ℃. ^{13}C NMR spectrum of 2 was nearly superimposable on that of 1 (Zou *et al*, 1993b) except an additional aceyl group of 1 (21.76, **CH_3**COO - ; 170.90, CH_3**COO** -) and some slight changes caused by the acetylation. The difference between 2 and 1 on their skeletons in ^{13}C NMR spectra was on ring E. Compared with ^{13}C NMR spectrum of 1, the signal of C - 19 of 2 was shifted upfield to 70.72 from 74.75 and the signals of C - 18 and C - 20 were shifted downfiels to 60.00 and 43.52 from 56.32 and 40.43 respectively. This fact could be readily understood when acylation shifts were taken into account (Terui *et al*, 1976). 2 was detected in the hydrolysate of 1 when 1 was treated with alkaline at room temperature. Accordingly the structure of 2 was elucidated as 7β, 19α, 28 - trhydroxyarbor - 9 (11) - en - 3 - one.

Rubiarbonone B (3), $C_{32}H_{50}O_5$ (M^+ at m/z 514), colorless needles, mp 98 ~ 100℃. Similar to 1, 3 could afford 2 also when treated with alkaline. This indicated that 3 was structyurally anal-

ogous to 1 with quite slight difference. Like that of 1, ^{13}C NMR of 3 also presented signals of an additional acetyl group (21.06, **CH_3**COO-; 170.72, CH_3**COO**-) when compared with that of 2. The position of the acetyl group in the molecule could be deduced by application of acylation shifts (Terui *et al*, 1976). The signal of C-28 was shifted downfield to 64.80 by 1.82 ppm while C-17 shifted upfield to 47.42 by 1.6 ppm on going from 2 to 3 indicating that the acetyl group was located at C-28. Thus the structure of 3 was elucidated as 28-acetoxyl-7β, 19α-dihydroxyarbor-9 (11)-en-3-one.

EXPERIMENT

General Melting points were measured on a kofler micromelting point apparatus and uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 NMR spectrometer (400 MHz and 100 MHz respectively) with deuterated pyridine as a solvent. Mass spectra were measured on VG Autospec-3000 spectrometer. Silica gel G (10~40 μm, Qingdao Marine Chemical Factory, China) and silanized silica gel (LiChroprep RP-8, 40~64 μm, Merck) were used for CC. All solvent systems for chromatography were homogeneous.

Plant material Roots of *R. yunnanensis* were collectedfrom Yunnan, China.

Extraction and isolation The ground roots of *Rubia yunnanensis* (10.0 kg) were extracted with MeOH (3×151) and then concentrated to dryness in vacuo. 1.0 kg extract was obtained. The extract was subject to activated charcoal chromatography and gradiently eluted with $CHCl_3$, EtOAc and $CHCl_3$-MeOH (v/v, 3/2). Compound 2 and 3 were obtained after chromatographed repeatedly with silica gel and silanized silica gel.

Rubiarbonone B (2) colorless needles, mp 155~157℃, $C_{30}H_{48}O_4$, MS m/z: 472 (M^+); ^1H NMR δ: 4.01 (td, 10, 5, H-7,), 5.45 (br d, 6, H-11), 2.34 (d, 10, H-18), 5.06 (td, 10, 3, H-19), 1.23 (s, CH_3-23), 1.02 (s, CH_3-24), 1.14 (s, CH_3-25), 1.3 (s, CH_3-26), 1.44 (s, CH_3-27), 4.23 and 4.09 (d, 11, 11-28), 0.96 (d, 5, CH_3-29), 1.08 (d, 6, CH_3-30); ^{13}C NMR: see Table 1.

Rubiarbonone A (1) was saponified with 2.5% $NaHCO_3$ and neutrlized with dilute AcOH and rubiarbone B (2) was detected by HPTLC.

Rubiarbonone C (3) colorless needles, mp 98~100℃, $C_{32}H_{50}O_5$, MS m/z: 514 (M^+); ^1H NMR δ: 3.97 (td, 10, 5, H-7), 5.40 (br d, 6, H-11), 2.27 (d, 10, H-18), 4.65 (td, 10, 3, H-19), 1.22 (s, CH_3-23), 1.03 (s, CH_3-24), 1.15 (s, CH_3-25), 1.17 (s, CH_3-26), 1.22 (s, CH_3-27), 4.63 and 4.30 (d, 12, 11-28), 0.86 (d, 5, CH_3-29), 0.96 (d, 6, CH_3-30), 2.06 (s, CH_3CO-28); ^{13}C NMR: see Table 1.

Rubiarbonone C (3) was saponified with 2.5% $NaHCO_3$ and neutralized with dilute AcOH and rubiarbone B (2) was detected by HPTLC.

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